AD-A043 617   MASSACHUSETTS UNIV AMHERST   F/G 11/10
                THE STRESS-OPTICAL COEFFICIENT AND AMORPHOUS ORDER. (U)
                SEP 74   R S STEIN, S D HONG   DAAG29-75-G-0135
UNCLASSIFIED   ARO-12942.3-C   NL

| OF |
AD
A043617

END
DATE
FILMED
9 -77
DDC

THE STRESS-OPTICAL COEFFICIENT AND AMORPHOUS ORDER

R. S. Stein and S. D. Hong
Polymer Research Institute
and Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Abstract

The calculated stress-optical coefficients obtained using the rotational isomer model and the principle of additivity of bond polarizability tensors give values of the segment polarizability anisotropy, $\Delta\Gamma_S$, in reasonable agreement with experimental values for swollen rubber networks. Furthermore, these values agree well with those obtained from streaming birefringence studies. Estimates of the effect of ordering in the amorphous state upon $\Delta\Gamma_S$ lead to values appreciably in excess of those found experimentally. The effect of swelling solvent on $\Delta\Gamma_S$ can be interpreted in terms of its role in separating chains from each other and in itself being oriented by the polymer chain. This model accounts for the observation that $\Delta\Gamma_S$ increases with increasing anisotropy of the swelling solvent. The value of $\Delta\Gamma_S$ found for networks swollen with an isotropic solvent is approximately, but not exactly, equal to the intrinsic anisotropy of the segment, $\Delta\Gamma_S$ found for undiluted networks arises in part from mutual orientation of segments by their neighbors. An additional cause comes from the anisotropy of the internal field arising from local order. All of these effects of the internal field arising from local order. All of these effects are interpretable in terms of relatively short-range interactions and do not require the relatively long-range ordering of a type proposed in some recent theories.

INTRODUCTION

The change in birefringence occurring when an amorphous polymer is deformed is an important observation which provides information concerning the state of order in amorphous solids. Since the

125

DDC
JUL 27 1977

(See 1473)A

presence of crystals appreciably affects the birefringence, we
shall restrict our considerations to those polymers which show no
equilibrium crystallinity at the temperature of study. Also,
because of the poorer understanding of glassy polymers as compared
with rubbery ones, we shall only consider systems above their T_g's.

The theory of birefringence of stretched rubbers was developed
by Kuhn and Grun [1] and by Treloar [2] on the basis of the same
procedure used for the development of the kinetic theory of
rubber elasticity. The model adopted was that of a chain composed
of anisotropic statistical segments which become oriented as the
rubber is stretched in a manner describable by the Gaussian
statistics of isolated chains in a cross-linked network, the cross-
linking points of which are subject to an affine transformation.
These theories lead to the expression for the stress-optical
coefficient

$$C = \frac{\Delta n}{\sigma} \frac{2\pi}{45kT} \frac{(\bar{n}^2 + 2)_2}{\bar{n}} \Delta\Gamma_s \tag{1}$$

where Δn is the birefringence of the uniaxially stretched sample
subjected to a stress σ (on unit area in the stretched state), k
is Boltzmann's constant, T is the absolute temperature, and $\bar{n}$ is
the avarage refractive index of the rubber. The anisotropy of the
statistical segment $\Delta\Gamma_s$ is given by

$$\Delta\Gamma_s = (b_1 - b_2)_2 \tag{2}$$

where b_1 and b_2 are the polarizabilities parallel and perpenducular,
respectively, to the axis of the segment.

Equation (1) is derived upon the assumption of the local
electrical field on a segment being given by the Lorenz-Lorentz
equation which implies that the environment of a segment is
optically isotropic. It also involves the assumption of tensor
additivity of polarizabilities of noninteracting segments.

The anisotropy of a segment may be related to the anisotropy of the constituents bonds, again assuming polarizability additivity using

$$\Delta \Gamma_s = \sum_i \left\{ (b_1 - b_2)_i \ [3 \cos^2 \theta_i - 1]/2 \right\} \tag{3}$$

where b_{1i} and $b_2 i$ are the polarizabilities of the i-th bond along and perpendicular to the bond axis and θ_i is the angle between the bond axis and the segment axis. Recently Flory [3] and Nagai [4] and co-workers have shown how to evaluate this sum in terms of the rotational isomer model giving rise to the equation

$$\Delta \Gamma_s = \frac{3}{2} \sum_i < \underset{\sim}{r}^T \hat{\underset{\sim}{\alpha}}_i \underset{\sim}{r} >_o / < r^2 >_o \tag{4}$$

where $\underset{\sim}{r}^T$ is the transpose (i.e., the row form) of the end-to-end vector $\underset{\sim}{r}$ and $\hat{\underset{\sim}{\alpha}}$ is the traceless tensor representing the anisotropy of the polarizability of bond i defined by

$$\hat{\underset{\sim}{\alpha}}_i = \underset{\sim}{\alpha}_i - \bar{\alpha}_i \underset{\sim}{E}_3 \tag{5}$$

where $\underset{\sim}{\alpha}_i$ is the polarizability tensor, $\bar{\alpha}_i$ is the mean polarizability, and $\underset{\sim}{E}_3$ is the identity matrix. The symbol $< >$ denotes averages over the free unperturbed chain. For hydrocarbons, this leads to the result that

$$\Delta \Gamma_s = A_{CC}(b_1 - b_2)_{CC} - A_{CH}(b_1 - b_2)_{CH} \tag{6}$$

where $(b_1 - b_2)_{CC}$ and $(b_1 - b_2)_{CH}$ are anisotropies of the CC and CH bonds and A_{CC} and A_{CH} are constants dependent upon molecular geometry. For tetrahedrally bonded hydrocarbon [5], $A_{CH}/ACC = 2$ while for the actual bond angles in polyethylene it is 1.88. Thus

$$\Delta \Gamma_s = A_{CC} \Delta \Gamma_{PM} \tag{7}$$

where $\Delta \Gamma_{PM}$ is the anisotropy of the polymethylene group given by

$$\Delta\Gamma_{PM} = (b_1 - b_2)_{CC} - 1.88 (b_1 - b_2)_{CH} \qquad (8)$$

Statistical calculations for polyethylene give a value of
$A_{CC} = 4.0 \pm 0.6$.

COMPARISONS BETWEEN EXPERIMENTAL AND THEORETICAL BIREFRINGENCE

Experimental measurements of $\Delta\Gamma_s$ of polyethylene have been
reported [6-8]. It is found that values are higher for unswollen
samples than for samples swollen with Decalin, the latter giving
$\Delta\Gamma_s = 4.0$ $\overset{\circ}{A}^3$ for $\phi_2 = 0.33$ corresponding to a value of $\Delta\Gamma_{PM} = 1.0$ $\overset{\circ}{A}^3$.
Theoretical values are dependent upon the choice of bond polari-
zabilities used in the calculation of $\Delta\Gamma_{PM}$ and are 1.47, 0.86, and
0.57 $\overset{\circ}{A}^3$ for the bond polarizabilities Denbigh [9], Clement and
Bothere [10], and LeFevre, Orr, and Ritchie [11], respectively.
The latter value, which was considered most reasonable for the
interpretation of light-scattering depolarization measurements in
n-paraffins [12], is somewhat small as compared with experimental
measurements and may result partly from the fact that the
concentration of polymer in the swollen gel used for the stress-
optical measurements was relatively high, and partly because
Decalin is not an isotropic solvent. Similar measurements have
been reported for poly(dimethylsiloxane) [8] but bond polarizability
information was not available to compare with experiment.

A study of the stress-optical coefficients of cis-1,4-polyisoprene
and cis-1,4-polybutadiene has been reported by Ishikawa and Nagai
[13] who also find that the SOC for the dry rubbers is greater than
that for the rubbers swollen with an isotropic solvent. For cis-
PBD, calculated values of $\Delta\Gamma_s$ range from 5.33 to 5.58 $\overset{\circ}{A}^3$ depending
on the parameters used in the statistical weight matrices and
using the Clement and Botherel polarizabilities [10] as compared
with experimental values of 5.8 $\overset{\circ}{A}^3$ on swollen samples and 7.5 $\overset{\circ}{A}^3$
for unswollen samples. Considerably smaller values of 3.92 and
4.09 $\overset{\circ}{A}^3$ are found using Denbigh's [9] or LeFebre's [11] values
of bond polarizabilities, respectively.

For cis-PIP, calculated values [13] range from 0.152 to 0.764 $\overset{\circ}{A}{}^3$ as compared with an experimental value of 0.72 $\overset{\circ}{A}$ calculated from data of Smith and Puett [14] on unswollen natural rubber.

For the above three cases, the agreement between experiment and theory is considered satisfactory, especially in view of the uncertainty concerning the values of anisotropic bond polarizabilities. It should be emphasized that the theory used is one which involves the orientation of an isolated chain with no correlation in orientation of segments on differing chains.

A systematic study of the stress-optical coefficients of samples of poly(1,4-butadienes) of differing cis content was undertaken by Fukada, Wilkes, and Stein [15], who confirmed the earlier reports of Ishikawa and Nagai [13] and Gent [16] that the values are appreciably affected by the swelling solvent used. For example, Fig. 1 shows a typical result [15] for the variation of birefringence with stress for high-cis cross-linked 1,4-poly-butadiene rubber swollen in a variety of solvents.

The value of the SOC increases with the anisotropy of the solvent and is least for the isotropic solvent, CCl_4. The values with CCl_4 are less than those for the unswollen polymer. It is suggested that adsorbed anisotropic solvents are oriented along with the polymer molecules and add to their anisotropy. Thus, for the unswollen polymers, the neighboring chains are adsorbed on each other and add to the SOC. This effect is diminished upon swelling with an isotropic solvent.

Another effect seen upon swelling is that both the stress and birefringence of the polymer obey Mooney-Rivlin-type equations

$$\sigma\phi_2^{1/3}/[\lambda^2 - \lambda^{-1}] = 2C_1 + 2C_2/\lambda \tag{9}$$

$$(\Delta n)\phi_2^{1/3}/[\lambda^2 - \lambda^{-2}] = B_1 + B_2/\lambda \tag{10}$$

where λ is the elongation ratio, ϕ_2 is the volume fraction of rubber, and the constants C_2 and B_2 represent deviations from
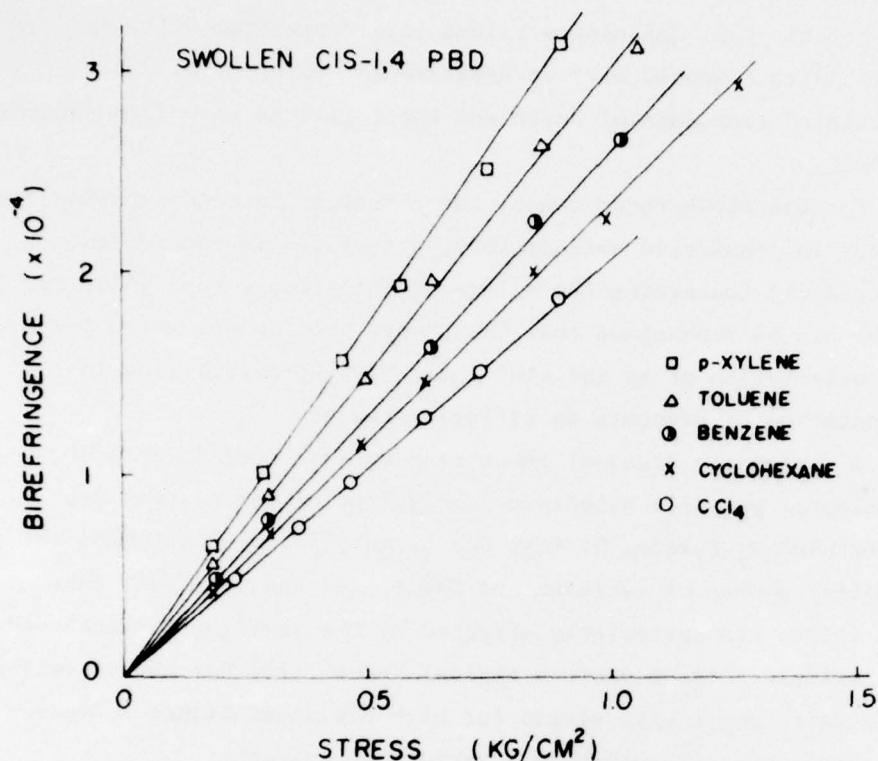
FIG. 1. The variation of birefringence with stress for high
cis cross-linked 1,4-polybutadiene rubber swollen in a variety
of solvents (From Ref. 15, Fig. 15).

ideal behavior. It is found that both C_2 and B_2 diminish to
essentially zero upon swelling, and one might wonder whether this
effect suggests chain packing or order. However, it has been found
that both C_2 [16-19] and B_2 [19] are substantially decreased for
unswollen networks which are cross-linked in the swollen state.
Figure 2 shows a typical birefringence Mooney-Rivlin-type plot [19]
obtained from samples of cis-1,4-polybutadiene cross-linked in
benzene solution at volume fractions ϕ_r designated in the figure.
(v_r in the figure corresponds to ϕ_2 in Eq. 9 and 10). Curves are
shown for measurements made on the subsequently dried polymer as
well as for samples then swollen with CCl_4 to values of ϕ_2 in the
range of 0.04 to 0.09. It is seen that even in the dry state the
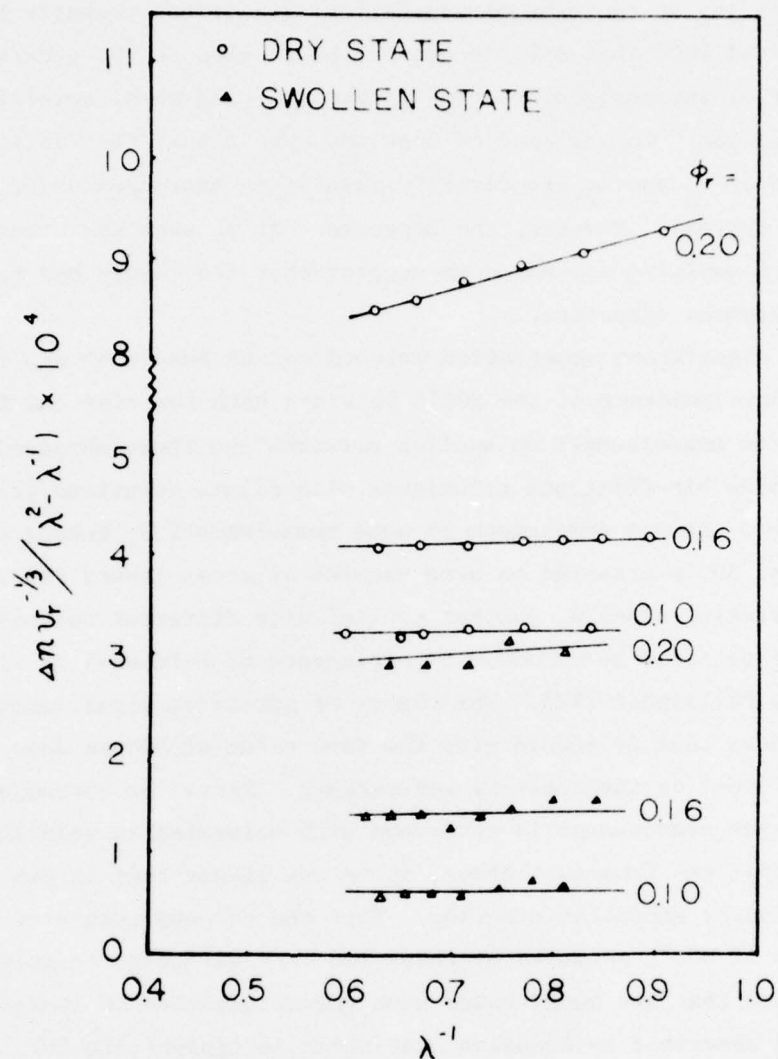slope of this plot is quite small, indicating values of B_2 of the

FIG. 2. Mooney-Rivlin type plots for the birefringence-strain relationship for solution vulcanized cis-1,4-polybutadiene. Samples were vulcanized in solution containing a volume fraction of rubber designated by ϕ_r in the figure. (The symbol v_r in the figure corresponds to ϕ_2 in the text.) (From Ref. 19, Fig. 2).

order of 0.2×10^{-4}. Since it is not likely that the molecular order in the dried network will depend upon the state of swelling at the time of cross-linking, it seems that this reduction is related to network topology differences dependent upon the state

of swelling at the time of cross-linking. It has recently been suggested [20] that differences may be related to the greater number of intramolecular cross-links occurring when cross-linking in solution. In any case it does not appear that the finite values of C_2 and B_2 are directly related to amorphous order for these systems. However, the dependence of B_1 upon the amount and kind of swelling solvent does suggest that its change may relate to amorphous structure.

A significant observation pointed out by Fukuda et al. [15] is the correspondence of the SOC's obtained both for cis- and trans-PBD from measurements on swollen networks and those obtained by streaming birefringence techniques with dilute solutions [21, 22]. Figure 3 shows a comparison of some measurements by Fukuda et al [15] of SOC's measured on some samples of cross-linked PBD samples of differing cis-1,4, content swollen with different solvents with values obtained by streaming birefringence by Poldubnyi et al. [21] and by Phillipoff [22]. The theory of streaming birefringence [23] indicates that it should give the same value of SOC as does the measurement on the cross-linked network. Since the streaming bire-fringence measurement is concerned with molecules in solution which are separated from each other, it is not likely that it can be affected by amorphous ordering. Thus the correspondence of the values of SOC's measured by these two very different techniques suggests that the model based upon the orientation of isolated chains described by Gaussian statistics is appropriate for moderately swollen networks and is inconsistant with any ordered structure. The question remains as to whether there is any increase in ordering in going from a swollen to an unswollen network. It should be noted that the difference between the values of the SOC in the unswollen and isotropically swollen state is relatively small, usually less than a factor of 2, and the en-hancement of the SOC in the dry state is comparable with that produced by the ordering of a solvent such as toluene in the swollen state. Consequently, we feel that while there may be some ordering
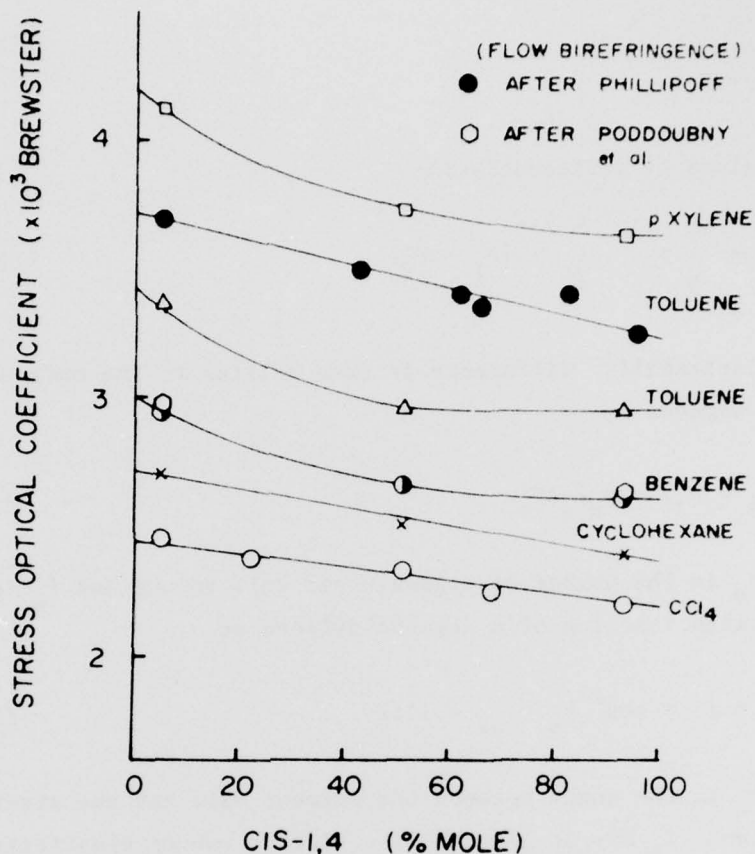
FIG. 3. The variation of the stress-optical coefficient of samples of cross-linked 1,4-polybutadiene with cis contant and for a number of swelling solvents as compared with streaming bire-fringence data. (From Ref. 15, Fig.21).

in dry polymers, relatively short-range ordering is sufficient to account for the observed result.

THE EFFECT OF AMORPHOUS ORDER ON THE STRESS-OPTICAL COEFFICIENT

In order to account for the possible effect of ordering on the SOC, we should examine the assumptions involved in the derivations of Eq. (1). It is based upon the Lorenz-Lorentz equation for the relationship between the refractive index, n, and the polarizability per unit volume P:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi P \qquad (11)$$

which gives by differentiating

$$\Delta n = \frac{2}{9} \pi \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (P_1 - P_2) \qquad (12)$$

The polarizability difference is then related to the anisotropy of the segment by

$$(P_1 - P_2) = N_s f_s \Delta \Gamma_s \qquad (13)$$

where N_s is the number of segments per unit volume and f_s is the orientation function of a segment defined as

$$f_s = [3 < \cos^2 \theta_s >_{av} - 1]/2 \qquad (14)$$

where θ_s is the angle between the segment axis and the stretching direction. f_s may be given by the kinetic rubber elasticity theory in the Gaussian approximation as

$$f_s = \frac{1}{5} \frac{N_c}{N_s} [\lambda^2 - \lambda^{-1}] \qquad (15)$$

where N_c is the number of chains per unit volume.

Equation (1) results from combining Eqs. (12) through (15) with the kinetic elasticity equation for the stress

$$\sigma = N_c kT [\lambda^2 - \lambda^{-1}] \qquad (16)$$

Ordering in the amorphous state will affect the derivation at two points: in the use of Eq. (11) for the internal field and in the use of Eq. (15) for segment orientation. Equation (15) is obtained in the Kuhn-Grün treatment [1] by calculating the

distribution function of segment orientations with respect to the displacement vector R using the Lagrange method of undetermined multipliers subjecting the distribution to the constraints of a fixed number of segments and a fixed length of R. This leads to a value for the orientation function f_R of segments with respect to R. The orientation function, f_s, is then obtained by convoluting this function with that of R with respect to the stretching direction. In this derivation, the segments are considered to have equal a priori probability of any orientation, and no interaction between segments on different chains is considered. This is obviously not so for an ordered amorphous phase. In a crystalline polymer, for example, a group of q segments on neighboring chains must be maintained parallel to each other. In this case the segment orientation function will be q times that given by Eq. (15). In the case of intermediate order, an average, $\bar{q}$, may be used which represents the number of segments surrounding a given segment whose orientation is correlated with that of the first segment. Since the SOC of the dry polymer was generally less than two times that of the swollen polymer, the factor q must be less than 2 if it is attributable to this cause. This is smaller by an order of magnitude or two than what would be expected on the basis of models which would have been proposed [24, 25] for ordered amorphous polymers.

The theory for the SOC for a swollen network of noninteracting chains [2] requires that the SOC should not vary with degree of swelling, provided that $\Delta\Gamma_s$ is not affected. If solvent molecules are oriented along with the polymer segment, the value of $\Delta\Gamma_s$ will be enhanced to give

$$\Delta\Gamma_s = \Delta\Gamma_s^o + \Delta\Gamma_\ell \qquad (17)$$

where $\Delta\Gamma_s^o$ is the anisotropy of the isolated polymer segment and $\Delta\Gamma_\ell$ is the additional anisotropy resulting from the orientation of the surrounding solvent. This is given by

$$\Delta\Gamma_\ell = \Delta\Gamma_\ell^{\,0} N_\ell \int f_\ell(r_{s\ell}) dr_{s\ell} \qquad (18)$$

$\Delta\Gamma_\ell^{\,0}$ is the intrinsic anisotropy of the solvent molecule, and N_ℓ is the number of solvent molecules per unit volume given by

$$N_\ell = (\rho_\ell N_o)/M_\ell \qquad (19)$$

where ρ_ℓ is the density of the solvent, N_o is Avagardro's number, and M_ℓ is the molecular weight of the solvent. $f_\ell(r_{s\ell})$ is the orientation function of the solvent molecules at a distance $r_{s\ell}$ from the segment with respect to the segment axis defined by

$$f_\ell(r_{s\ell}) = [3 < \cos^2 \theta_{s\ell} >_r - 1]/2 \qquad (20)$$

where $\theta_{s\ell}$ is the angle between the segment axis and the optic axis of the solvent. The integral is over all lengths and orientations of $r_{s\ell}$. The symbol $< >$ designates averaging at constant $r_{s\ell}$.

$$< \cos^2 \theta_{s\ell} >_r = \frac{\int_o^\pi P(\theta_{s\ell}, r_{s\ell}) \cos^2 \theta_{s\ell} \sin \theta_{s\ell} d\theta_{s\ell}}{\int_o^\pi P(\theta_{s\ell}, r_{s\ell}) \sin \theta_{s\ell} d\theta_{s\ell}} \qquad (21)$$

where $P(\theta_{s\ell}, r_{s\ell})$ is the probability of orientation at angle $\theta_{s\ell}$ for a solvent molecule separated from the segment by distance $r_{s\ell}$. This may be described by a Boltzmann distribution

$$p(\theta_{s\ell}, r_{s\ell}) = K \exp[-V(\theta_{s\ell}, r_{s\ell})/kT] \qquad (22)$$

where $V(\theta_{s\ell}, r_{s\ell})$ is the potential for interaction between the polymer segment and the solvnet molecule which depends upon inter-molecular forces and decreases rapidly with their separation.

It is evident from this treatment that $\Delta\Gamma_s$ should increase with increasing solvent anisotropy, $\Delta\Gamma_\ell$, and should be a minimum for

isotropic solvents. However, it must be realized that

$$\Delta\Gamma_\ell^{\,O} = (\Delta\Gamma_\ell^{\,O})_{inh} + (\Delta\Gamma_\ell^{\,O})_{ind} \tag{23}$$

where $(\Delta\Gamma_\ell^{\,O})_{inh}$ is the inherent anisotropy of the isolated solvent
molecule and $(\Delta\Gamma_\ell^{\,O})_{ind}$ is the induced anisotropy arising from the
dipole moment induced in the solvent by the dipole moment of the
segment. This, of course, depends upon the solvent polarizability.
Consequently, even if $(\Delta\Gamma_\ell^{\,O})_{inh} = 0$ as with CCl_4, it may be that
there is a finite $(\Delta\Gamma_\ell^{\,O})_{ind}$ so that $\Delta\Gamma_s$ may not equal $\Delta\Gamma_s^{\,O}$ as is
usually assumed.

To some extent, the enhancement of $\Delta\Gamma_s$ for unswollen polymers
which arises from local order may be treated in the above manner
in which the segments of neighboring chains play the role of
ordered solvent molecules.

EFFECT OF INTERNAL FIELD

The refractive index of a material is realted to its polarization
by

$$n^2 - 1 = 4\pi \underline{P}/\underline{E} \tag{24}$$

where $\underline{E}$ is the applied field. $\underline{P}$ in turn is given by

$$\underline{P} = N\alpha\underline{E}_{eff} \tag{25}$$

where N is the number of molecules/cm^3 having polarizability α,
and $\underline{E}_{eff}$ is the effective field acting on the molecule. This is
realted to the applied field by

$$\underline{E}_{eff} = \underline{E} + \underline{E}_{int} \tag{26}$$

where E_{int} is the internal field arising from the polarization of
surrounding molecules. Lorentz calculates this as the field
arising from the polarization charge on the surface of a spherical

cavity of a dielectric which leads to the result

$$\underline{E}_{eff} = \frac{n^2 + 2}{3} \underline{E} \tag{27}$$

The use of this Lorentz field in Eqs. (24) and (25) leads to the
Lorenz-Lorentz equation. This equation is satisfactory for gases
or isotropic liquids but its application to an anisotropic crystal
is incorrect. We believe that its erronious use in relating the
polarizabilities to the refractive index of n-paraffin crystals has
led to the very low value of Γ_{PM} of 0.3 $\overset{\circ}{A}^3$ [26] as compared with
the higher value of 1.47 obtained by Denbigh [9] from gas-phase
light-scattering depolarization measurements [27]. It is not
reasonable to accommodate an elongated polyethylene chain within a
spherical cavity, and Stein has proposed [27] an alternate approach
utilizing a cylindrical cavity within which the internal field
factor κ_i is defined by

$$(\underline{E}_{eff})_i = \kappa_i \underline{E}_o \tag{28}$$

is different parallel and perpendicular to the axis of the cylinder
and depends upon its axial ratio. It was shown that with reasonable
values of the axial ratio, the difference between the two values
of $\Delta\Gamma_{PM}$ may be understood.

More recently, Hong and Stein [28] have developed a theory for
the internal field within a polyethylene crystal based upon a
summation over the contribution from dipolar fields of neighboring
molecules. A polyethylene chain in a crystal is replaced by a
cylinder with differing longitudinal and transverse polarizabilities
located at the position of the real chains in the unit cell of the
polyethylene crystal. The induced field at position p within a
crystal arising from a point dipole at position r_{ip} removed from
p is given by

$$E_{ip} = \frac{3(m_i \cdot r_{ip})}{r_{ip}^5} \, r_{ip} - \frac{m_i}{r_{ip}^3} \tag{29}$$

The total internal field at p is then given by

$$(E_{int})_p = \sum_i E_{ip} \tag{30}$$

The dipole moment m_i is obtained from the total field at i from

$$m_i = |\alpha_i| E_i \tag{31}$$

where $|\alpha_i|$ is the polarizability tensor at i. For a uniaxially polarizable element, Eq. (31) becomes

$$m_i = \delta_i (E_i \cdot a_i) \, a_i + \alpha_{2i} E_i \tag{32}$$

where δ_i is the anisotropy of polarizability of the i-th volume element, $(\alpha_{1i} - \alpha_{2i})$, and a_i is a unit vector along the principal polarizability axis. E_i is obtained in turn by adding to the external field, the internal field at i of the molecules surrounding point i.

This procedure is carried out by summing over an infinite crystal using iteration. In this way, the ratio of the dipole moment to the externally applied field may be determined leading to an expression for the internal field factor

$$\kappa_i = \frac{m_i}{E_o |\alpha|} \tag{33}$$

This procedure is extended to a disordered structure, using the statistical segment modification. For this purpose Eqs. (29) and (3) are replaced by an integration over a segment distribution function

$$E_p = \int P(r_p, a) \left\{ \frac{3(m \cdot r_p)}{r_p^5} r_p - \frac{m}{r_p^3} \right\} dr_p \qquad (34)$$

where $P(r_p, a)$ is the probability that a segment will lie at a distance r_p from p and be oriented in the direction a. The solution of this equation requires assuming some form for the segment distribution function. This function could be expanded in spherical harmonics where the coefficients serve as correlation functions in a manner similar to that used in the theory of light scattering from systems having nonrandom orientation correlations [29, 30]. The coefficients in this expansion serve as correlation functions which describe how molecular order decreases with increasing molecular separation. These contain correlation distances which serve as measures of the size of ordered regions. In this manner it would be possible to account for the internal field effects.

Let the reference molecule at position p be oriented in the Z direction and consider the effect of a second molecule, i, located at a vector distance r_{ip} having angular coordinates ω and ψ (Fig. 4) which is oriented with its principal polarizability axis a_i at angles β and γ. For an applied field in the Z direction, Eq. (29) gives for the components of internal field at p

$$\begin{aligned}
E_{ix,p} = (E/r^3) \Big\{ &3\delta_i (\sin \omega \cos \psi)^2 (\sin \beta \cos \beta \cos \gamma \\
&+ 3\delta_i (\sin^2 \omega \sin \psi \cos \psi)(\sin \beta \cos \beta \sin \gamma) \\
&+ 3[\bar{\alpha}_i + \delta_i (\cos^2 \beta - (1/3))] \sin \omega \cos \omega \cos \psi \\
&- \delta_i \sin \beta \cos \beta \cos \delta \Big\}
\end{aligned} \qquad (35)$$

$$\begin{aligned}
E_{iy,p} = (E/r^3) \Big\{ &3\delta_i (\sin^2 \omega \sin \psi \cos \psi)(\sin \beta \cos \beta \cos \gamma) \\
&+ 3\delta_i (\sin \omega \sin \psi)^2 (\sin \beta \cos \beta \sin \gamma) \\
&+ 3[\bar{\alpha}_i + \delta_i (\cos^2 \beta - (1/3))] \sin \omega \cos \omega \sin \psi \\
&- \delta_i \sin \beta \cos \beta \sin \gamma \Big\}
\end{aligned} \qquad (36)$$
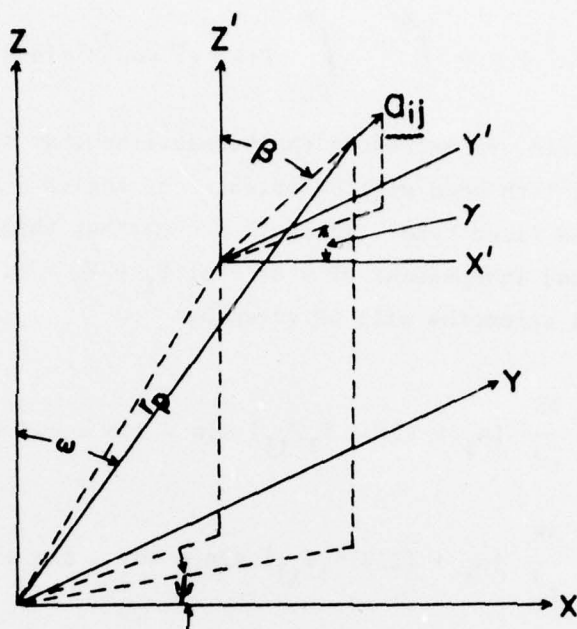
FIG. 4. The angles ω and ψ defining the orientation of the vector r_p and the angles β and γ defining the orientation of the principal polarizability axis of the i-th bond.

and

$$E_{iz,p} = (E/r^3) \left\{ 3 \delta_i (\sin \omega \cos \omega \cos \psi)(\sin \beta \cos \beta \sin \gamma) \right.$$

$$+ 3 \delta_i (\sin \omega \cos \omega \sin \psi)(\sin \beta \cos \beta \cos \gamma)$$

$$\left. + [\bar{\alpha}_i + \delta_i (\cos^2 \beta - (1/3))] [3 \cos^2 \omega - 1] \right\} \qquad (37)$$

The average internal field components at the origin is then found by averaging over angles. It is convenient to define the averages

$$F_1 = < \sin \beta \cos \beta \cos \gamma > = \int_0^{2\pi} \int_0^{\pi} P(\beta, \gamma) \sin^2 \beta$$

$$\cos \beta \cos \gamma \, d\beta d\gamma \qquad (38)$$

$$F_2 = < \sin \beta \cos \beta \sin \gamma > = \int_0^{2\pi} \int_0^{\pi} P(\beta, \gamma) \sin^2 \beta$$

$$\cos \beta \sin \gamma \, d\beta d\gamma \qquad (39)$$

and

$$F_3 = <\cos^2 \beta> = \int_0^{2\pi} \int_0^{\pi} P(\beta, \gamma) \cos^2 \beta \sin \beta \, d\beta d\gamma \quad (40)$$

The function $P(\beta, \gamma)$ expresses the probability that the polarizability axis a of the i-th bond will be oriented at angles β and γ with respect to the first bond. We shall assume that this is cylindrically symmetrical and independent of γ so that $F_1 = F_2 = 0$. Thus the average field strengths will be given by

$$\bar{E}_{i,xp} = \frac{3E}{r^3} [\alpha_i + (2/3) \delta_i F_{ij}] \sin \omega \cos \omega \cos \psi \quad (41)$$

$$\bar{E}_{i,yp} = \frac{3E}{r^3} [\alpha_i + (2/3)\delta_i F_{ij}] \sin \omega \cos \omega \sin \psi \quad (42)$$

and

$$\bar{E}_{i,zp} = \frac{E}{r^3} [\alpha_i + (2/3)\delta_i F_{ij}] [3 \cos^2 \omega - 1] \quad (43)$$

where

$$F_{ij} = [3 <\cos^2 \beta> - 1]/2 \quad (44)$$

The function F_{ij} characterizes the correlation of orientation of two molecules separated by vector distance r_{ij} and diminishes with increasing magnitude of r.

The total average field at point p is then found by summing over all contributions from bonds i to give

$$\bar{E}_p = \sum_i \bar{E}_{ip} = \bar{E}_{xp} i + \bar{E}_{yp} j + \bar{E}_{zp} k \quad (45)$$

If we further assume that there is cylindrical symmetry of bond distribution in ψ, then $\bar{E}_{xp} = \bar{E}_{yp} = 0$ so

$$\bar{E}_p = \bar{E}_{zp} \, k \tag{46}$$

where

$$\bar{E}_{zp} = \sum_i (E/r^3) \left\{ [\bar{\alpha}_i + (2/3)\delta_i F_{ij}] \, [3 \cos^2\omega - 1] \right\} \tag{47}$$

A similar treatment for the case where the applied field is along the X (or the Y) axis leads to

$$\bar{E}_p = \bar{E}_{xp} \, i \tag{48}$$

where

$$\bar{E}_{xp} = \sum_i (E/r^3) \left\{ [\bar{\alpha}_i - (1/3)\delta_i F_{ij}][3 \sin^2\omega \cos^2\psi - 1] \right\} \tag{49}$$

The evaluation of the internal field then requires the assumption of some form for F_{ij}. Rather than assuming an empirical function to represent correlation in a partially ordered amorphous structure such as that portrayed in Fig. 5, we shall idealize it as a two-phase model shown in Fig. 6 consisting of 1) cylindrical domains within which there is crystal-like order where $F_{ij} = 1$ surrounded by 2) a random phase where there is complete disorder where $F_{ij} = 0$. Consequently Eq. (48) becomes

$$\bar{E}_{zp} = E \left\{ \sum_{ord} [(1/r^3)(3 \cos^2\omega - 1)\alpha_{||}] + \sum_{dis} [(1/r^3) (3 \cos^2\omega - 1) \alpha] \right\}$$

$$= (\bar{E}_{zp})_{ord} + (\bar{E}_{zp})_{dis} \tag{50}$$

while Eq. (49) gives

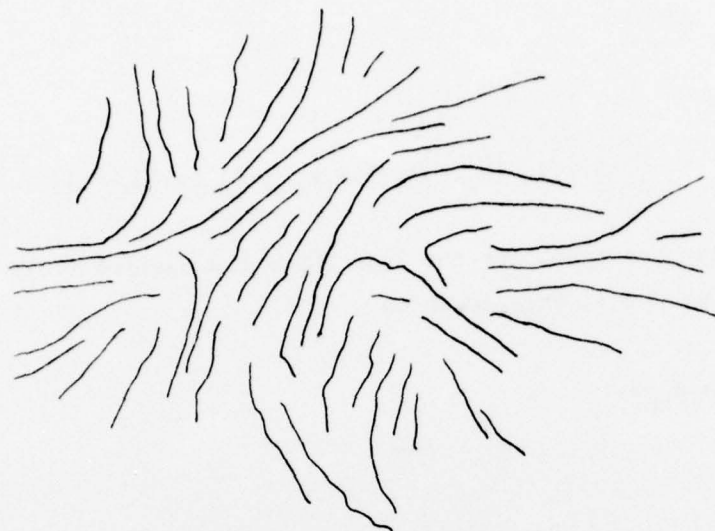FIG. 5. The partially ordered amorphous phase in which closely spaced chains tend to lie parallel to each other.

$$\bar{E}_{xp} = E \left\{ \sum_{ord} [1/r^3](3 \sin^2 \omega \cos^2 \psi - 1) \alpha_\perp] + \sum_{dis} [1/r^3] \right.$$

$$\left. (3 \sin^2 \omega \cos^2 \psi - 1) \bar{\alpha}] \right\}$$

$$= (\bar{E}_{xp})_{ord} + (\bar{E}_{xp})_{dis} \tag{51}$$

where all of the molecules are considered identical and

$$\alpha_{||} = \bar{\alpha}_i + (2/3) \delta_i \tag{52}$$

$$\alpha_\perp = \bar{\alpha}_i - (1/3) \delta_i \tag{53}$$

To evaluate $(\bar{E}_{zp})_{ord}$ and $(\bar{E}_{xp})_{ord}$, we may use the results of the previous treatment [28] for crystalline polyethylene which gives
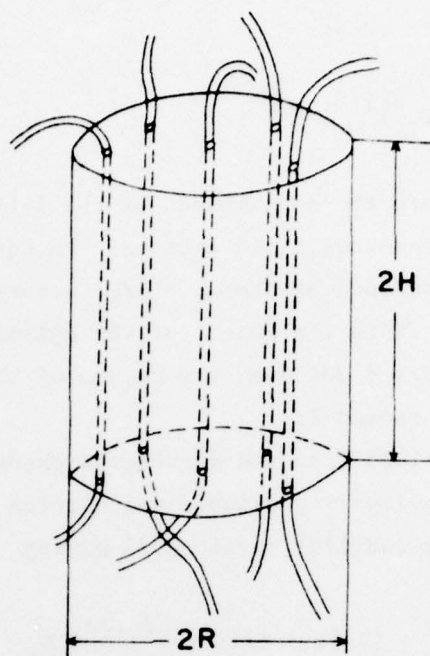
FIG. 6. The idealized two-phase model consisting of cylindrical ordered regions imbedded in a disordered matrix.

$$(\bar{\underset{\sim}{E}}_{zp})_{ord} = \underset{\sim}{E} \sum_i \left\{ (2/\varepsilon_{zi} C_i^2) (\sin^3 \omega_i = \sin \omega_i) \alpha_{||} \right\}$$

$$= K_z' \underset{\sim}{E} \alpha_{||} \tag{54}$$

and

$$(\bar{\underset{\sim}{E}}_{xp})_{ord} = \underset{\sim}{E} \sum_i \left\{ (2\, x_i^{2/\varepsilon}{}_{xi} C_i^4)(3 \sin \omega_i - \sin^3 \omega_i) \right.$$

$$\left. - 2 \sin \omega_i / \varepsilon_{xi} C_i^2 \right\} \alpha_\perp$$

$$= K_x' \underset{\sim}{E} \alpha_\perp \tag{55}$$

where ϵ is the dielectric constant (assumed constant as ϵ_z and ϵ_x) and C_i is defined as

$$C_i{}' = (x_i{}^2 + y_i{}^2)^{1/2} \tag{56}$$

where x_i and y_i are the coordinates of the i-th molecule and $K_z{}'$ and K_x are the internal field factors. In Eqs. (54) and (55), the angle ω_i is defined as $\tan \omega_i = H/C_i$ according to our previous treatment, where 2H is the height of the cylindrical cavity. The summation was carried out over the volume of the cylindrical cavity of height 2H and radius R.

The interal field from the disordered phase is evaluated utilizing the previously published calculation of the internal field within a cylindrical cavity [27] giving

$$(\bar{E}_{zp})_{dis} = n^2 - 1) \ [1 - f/(1 + f^2)^{1/2}] \ \underset{\sim}{E}_o$$
$$= K_z{}'' \ \underset{\sim}{E}_o \tag{57}$$

and

$$(\bar{E}_{xp})_{dis} = [(n^2-1)/2] \ [f/(1 + f^2)^{1/2}] \ \underset{\sim}{E}_o$$
$$= K_x{}'' \ \underset{\sim}{E}_o \tag{58}$$

where
$$f = H/R \tag{59}$$

is the axial ratio of the cavity. n is the average refractive index of the polymer.

The total internal field at p is then

$$\bar{E}_{xp} = K_z{}' \ \alpha_{||} \underset{\sim}{E}_{eff,z} + (K_z{}'' / \epsilon_z) \ \underset{\sim}{E}_o \tag{60}$$

and

$$\bar{E}_{xp} = K_z' \alpha_\perp E_{eff,x} + (K_z''/\varepsilon_x) E_o \qquad (61)$$

The dielectric constants must be introduced into the second terms to account for the modification of the polarization field of the disordered amorphous phase by the medium within the cavity. Since the effective field is the sum of the applied field and internal field, it must be evaluated by an iteration process leading to

$$E_{eff,z} = \left[\frac{1}{1 - k_z' \alpha_{||}} \right] \left[1 + \frac{K_z''}{\varepsilon_z} E_o \right] \qquad (62)$$

$$= K_z E_o$$

and

$$E_{eff, x} = \left[\frac{1}{1 - K_x' \alpha_\perp} \right] \left[1 + \frac{K_x''}{\varepsilon_x} E_o \right] \qquad (63)$$

The effective anisotropy may then be calculated from

$$\bar{\Lambda} = K_z \alpha_{||} - K_x \alpha_\perp \qquad (64)$$

This calculated anisotropy will include the total contribution of all the molecules within the ordered region which are subjected to the internal field which is modified by the ordering. Thus the increase in anisotropy from ordering obtained in this way is a consequence of both enhancement of anisotropy arising from the association of molecules within the aggregates as well as the effects arising from the influence of ordering upon the internal field.

The anisotorpy has been calculated taking the dimensions of the ordered region as an adjustable parameter. We have modified the preceding procedure in what we have allowed for some disorder in

the ordered region, taking it as a paracrystal in which the chains are parallel to each other but where they may deviate from their ideal lattice points in a direction perpendicular to the chain (cylinder) axis. Two cases were considered: one where the fluctuation in the x and y directions (parallel to the a and b crystal axes of the polyethylene unit cell) was ± 1 and ± 0.5 Å, respectively, and a second where the fluctuations are assymetric and are between -1 and $+2$ Å in the a-axis direction and -0.75 to $+1.25$ Å in the b-axis direction. The paracrystalline lattices possessing such fluctuations were generated using a random number routine with a computer, assuming that all values of lattice parameters within the prescribed limits may occur with equal probability. Polarizabilities were calculated for the parameters of the polyethylene unit cell where $a = 7.40$ Å, $b = 4.93$ Å, and $c = 2.534$ Å. The values of bond polarizabilities for the bonds within a crystal corrected for the internal field effect, which were proposed in our earlier publication were employed. The dielectric constant was assumed to be equal to the macroscopic dielectric constant of the crystal along each of the three crystal axes.

In this way the curves of Fig. 7 were obtained which show the variation of the effective anisotropy of the statistical segment defined by Eq. (64) as a function of the diameter of the cylindrical ordered region for various values of its axial ratio. As expected, the anisotropy increases with the size of the ordered region and does so more rapidly as the axial ratio of the ordered region becomes greater. The increase is more pronounced for a more disordered lattice.

The values are compared with the range of values calculated from experimental stress-optical coefficients. In making such a comparison, one must consider that the value of $\Delta\Gamma_s$ obtained from the stress-optical coefficient using Eq. (1) involves the assumption of the Lorentz field of Eq. (27) and is therefore not strictly
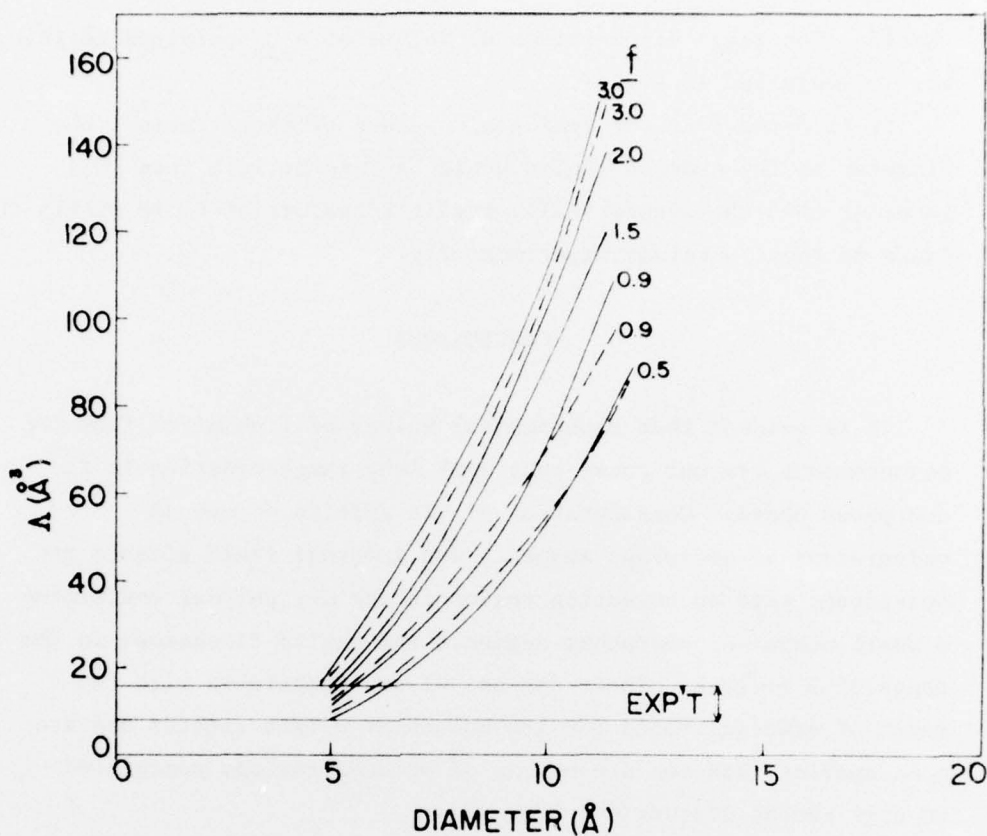
FIG. 7. The variation of the effective anisotropy of the statistical segment of polyethylene with the diameter of the cylindrical ordered region for several values of its axial ratio. Calculations were carried out for paracrystalline structure of the ordered region assuming (a) $\Delta a = + 1$ Å and $\Delta b = + 0.5$ Å (dashed line) and (b) -1 Å $> \Delta a > 2$ Å and $- 0.75$ Å $> \Delta b > 1.25$ Å (solid line). Values are compared with the range of calculated experimental values of Λ

comparable with that given by Eq. (64). Thus one whould actually compare the quantity

$$\Lambda_{exp} = \frac{(\bar{n}^2 + 2)^2}{9} (\Delta \Gamma_s)_{exp} \tag{65}$$

which is the product of the experimental segment anisotropy and the internal field correction factor with Eq. (64) rather than $\Delta \Gamma_s$

itself. The range of experimental values of Λ_{exp} obtained in this way is indicated in Fig. 7.

It is noted that for reasonable values of axial ratios, the diameter of the ordered region would have to be less than 10 Å in order that the theoretically predicted values of Λ lie within the range of those obtained experimentally.

CONCLUSIONS

It is evident that experimental values of Γ obtained from SOC measurements are not consi tent with long-range ordering in the amorphous phase. Consideration of the effects of mutual orientation of amorphous segments and internal field effects are consistent with an orienting region in the dry polymer containing a small number of amorphous segments and having dimensions in the range of 5 to 10 Å. These dimensions are comparable with the range of ordering found for low molecular weight liquids and are much smaller than the dimensions of ordered regions postulated in some recent discussions [24, 25].

Acknowledgments

REFERENCES

[1]   W. Kuhn and F. Grün, Kolloid-Z., 101, 248 (1942)
[2]   L. R. G. Treloar, Trans. Faraday Soc., 43, 277 (1947);
       50, 881 (1954); The Physics of Rubber Elasticity,
       2nd ed., Oxford Univ. Press, oxford, 1967.
[3]   P. J. Flory, Statistical Mechanics of Chain Molecules,
       Wiley Interscience, New York, 1969; P. J. Flory,
       R. L. Jernigan, and A. Tonelli, Macromolecules, 5, 550
       (1972).
[4]   K. Nagai, J. Chem. Phys., 40, 2818 (1964); 49, 4212 (1960);
       K. Nagai and T. Ishikawa, Ibid., 45, 3128 (1966).

[5]   R. P. Smith and E. M. Mortensen, Ibid., 32, 502 (1960).

[6]   A. N. Gent and V. V. Vickroy, Jr., J. Polym. Sci., A2,
      5, 47 (1967); A. N. Gent and T. H. Kuan, Ibid., 9, 927
      (1971).

[7]   D. W. Saunders, D. R. Lightfoot, and D. A. Parson, Ibid.,
      6, 1183 (1968).

[8]   M. H. Liberman, Y. Abe, and P. J. Flory, Macromolecules,
      5, 550 (1972).

[9]   K. G. Denbigh, Trans. Faraday Soc., 36, 936 (1940).

[10] C. Clement and P. Botherel, J. Chim. Phys. Phys. Chim.
      Biol., 61,878, 1262 (1964); C. R. Acad. Sci., 258, 4757
      (1964).

[11] R. J. W. LeFevre, B. J. Orr, and G. L. D. Ritchie, J.
      Chem. Soc., B, 1966, 273; R. L. W. LeFevre, Adv. Phys.
      Org. Chem., 3, 1 (1965).

[12] G. D. Patterson and P. J. Flory, Trans. Faraday Soc.,
      68, 1098 (1972).

[13] T. Ishikawa and K. Nagai, J. Polym. Sci., A-2, 7, 1123
      (1969).

[14] K. J. Smith and D. Puett, J. Appl. Phys., 37, 364 (1966).

[15] M. Fukuda, G. L. Wilkes, and R. S. Stein, J. Polym. Sci.,
      A-2, 9, 1417 (1971).

[16] A. N. Gent, Macromolecules, 2, 262 (1961)

[17] C. Price, G. Allen, F. deCandia, M. C. Kirkham, and A.
      Subramanian, Polymer, 11, 486 (1970); C. Price, K. A. Evans,
      and F. deCandia, Ibid., 14, 338 (1973).

[18] J. E. Mark, J. Am. Chem. Soc., 92, 7252 (1970); C. U. Yu
      and J. E. Mark, Macromolecules, 6, 751 (1973).

[19] C. S. M. Ong and R. S. Stein, J. Polym. Sci., Polym.
      Phys., Ed., 12, 1599 (1974).

[20] A. E. Tonelli and E. Helfand, Macromolecules, 7, 59 (1974).

[21] I. Ya. Poldubnyi, Ye. G. Erenburg, and M. A. Yeremina,
      Vysokomol. Soedin., A10, 1381 (1968).

[22] W. Phillipoff, Private Communication, 1970.

[23] K. Nagai, J. Phys. Chem., 74, 411 (1970).

[24] G. S. Y. Yeh, Pure Appl. Chem., 31, 65 (1972); CRC Crit.
      Rev. Macromol. Sci., 1, 173 (1972).

[25] W. Pechold, IUPAC Prepr., 1971, 789; W. Pechold, M. E. T.
      Hauber, and E. Liska, Kolloid Z. Z., 251, 818 (1973).

[26] C. W. Bunn and R. Daubeny, Trans. Faraday, Soc., 50, 1173
      (1954)

[27] R. S. Stein, J. Polym. Sci., A-2, 7, 1021 (1969).

[28] S. D.Hong, C. Chang, and R. S. Stein, J. Polym. Sci.,
      Polym. Phys. Ed. 13, 1447 (1975).

[29] R. S. Stein, P. F. Erhardt, S. B. Clough, and G. Adams,
      J. Appl. Phys., 37, 3980 (1966).

[30] J. J. van Aartsen, Polymer Networks, Structure and
      Mechanical Properties (A. J. Chompff and S. Newman, eds.)
      Plenum, New York, 1971, p. 307.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 12942.3-C	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE STRESS-OPTICAL COEFFICIENT AND AMORPHOUS ORDER		5. TYPE OF REPORT & PERIOD COVERED Reprint
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R. S. Stein S. D. Hong		8. CONTRACT OR GRANT NUMBER(s) DAAG29-75-G-0135
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Massachusetts Amherst, Mass. 01002		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 1976
		13. NUMBER OF PAGES 28 p.
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Stresses	Anisotropy
Optics	Rubber
Coefficients	Birefringence
Polarization	Amorphous materials
Solvents	Polymers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The calculated stress-optical coefficients obtained using the rotational isomer model and the principle of additivity of bond polarizability tensors give values of the segment polarizability anisotropy, $\Delta\Gamma_s$, in reasonable agreement with experimental values for swollen rubber networks. Furthermore, these values agree well with those obtained from streaming birefringence studies. Estimates of the effect of ordering in the amorphous state upon $\Delta\Gamma_s$ lead to values appreciably in excess of those found experimentally. The

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

ARO 12942.3-C

20. ABSTRACT CONTINUED

effect of swelling solvent on $\Delta\Gamma_s$ can be interpreted in terms of its role in separating chains from each other and in itself being oriented by the polymer chain. This model accounts for the observation that $\Delta\Gamma_s$ increases with increasing anisotropy of the swelling solvent. The value of $\Delta\Gamma_s$ found for networks swollen with an isotropic solvent is approximately, but not exactly, equal to the intrinsic anisotropy of the segment, $\Delta\Gamma_s$ found for undiluted networks arises in part from mutual orientation of segments by their neighbors. An additional cause comes from the anisotropy of the internal field arising from local order. All of these effects of the internal field arising from local order. All of these effects are interpretable in terms of relatively short-range inter-actions and do not require the relatively long-range ordering of a type proposed in some recent theories.